# Copper(II) Complexes with 2,2′-Biimidazole. Preparation and Crystal Structure Determination of a Complex of Stoichiometry $Cu_{1.5}Cl_3(H_2bim)_2$ ($H_2bim$ = 2,2′-biimidazole)

ALESSANDRO BENCINI and FABRIZIO MANI

*Dipartimento di Chimica, Università di Firenze, Florence, Italy*

(Received May 3, 1988)

## Abstract

By reacting 2,2′-biimidazole and copper(II) chloride in aqueous HCl we obtained the complex $CuCl_2(H_2bim)$ as the main product and a compound with stoichiometry $Cu_{1.5}Cl_3(H_2bim)_2$ as a byproduct. The structure of the latter compound has been determined by X-ray analysis: monoclinic, $a = 794.0(3)$, $b = 3146.8(6)$, $c = 722.9(4)$ pm, $\beta = 114.2(1)°$, space group $P2_1/c$. The compound actually contains two species, namely $[Cu(H_2bim)_2]Cl_2$ and $[CuCl_2(H_2bim)]$ in a 1:2 molar ratio.

## Introduction

The synthesis of some 3-d metal complexes with either neutral or deprotonated 2,2′-biimidazole was reported for the first time in the sixties [1]. Since then, the coordination properties of this ligand have been rarely investigated [2]. Recently there has been a renewed interest in the coordination chemistry of 2,2′-biimidazole. This is due to the current interest in finding new systems which can transmit exchange interactions between paramagnetic centers, with the aim of understanding the physical mechanisms which determine the size and the sign of the exchange interactions and of being able to design the synthesis of the so called 'molecular magnets' [3]. Moreover, the 2,2′-biimidazole moiety is of importance as a biomimetic ligand because the imidazole ring of histidine has been frequently found in a variety of proteins and metalloenzymes [4].

In order to model the physical and chemical behaviour of natural systems, either unsubstituted or substituted 2,2′-biimidazole has been used as a ligand to design synthetic analogues of metalloenzymes. In some cases the structure of the complexes has been investigated by means of X-ray diffraction methods [5].

As far as copper(II) and 2,2′-biimidazole are concerned, the only structures which have been investigated by X-ray analysis are those of the mononuclear bis(4,4′,5,5′-tetramethyl-2,2′-biimidazole)copper(II) dinitrate [5b] and of the dinuclear $\mu$-2,2′-biimidazolato-bis(1,1,4,7,7-pentamethyldiethylenetriamine)dicopper(II) tetraphenylborate [5a] which contains the dianionic 2,2′-biimidazolato as a bridge.

Now we report on the synthesis and the crystal structure determination of a new complex of copper(II) with the neutral 2,2′-biimidazole having the stoichiometry $Cu_{1.5}Cl_3(H_2bim)_2$ ($H_2bim$ = 2,2′-biimidazole).

## Experimental

### Materials and Preparation

All reagents and solvents were of reagent grade purity and used as received. The 2,2′-biimidazole was prepared according to published procedures [1, 5]. The ligand and hydrated $CuCl_2$ were reacted in aqueous HCl solution. Accordingly, 1.00 mmol of the hydrated $CuCl_2$ salt dissolved in water was added to 2.00 mmol of $H_2bim$ suspended in water. To the resulting mixture enough concentrated HCl solution was added until the suspension became clear. The total amount of the solution was 20 $cm^3$. The solution was reduced to half volume by boiling and 10 $cm^3$ water added. This operation was repeated twice and the resulting solution was allowed to stand overnight at room temperature. A first crop of microcrystalline green compound having the stoichiometry $CuCl_2(H_2bim)$ was thus obtained. The compound was filtered, washed with ethanol, ethyl ether and dried *in vacuo*. *Anal.* Calc. for $CuCl_2C_6H_6N_4$: C, 20.86; H, 2.25; N, 26.83; Cu, 23.66. Found: C, 21.1; H, 2.20; N, 27.1; Cu, 23.3%. The filtrate was allowed to slowly evaporate at room temperature for a month, after which a mixture of two crystalline compounds was obtained. These were washed with ethanol, diethyl ether and dried *in vacuo*. The two types of crystals were separated by hand-picking. Most of the crystals correspond again to the formula $CuCl_2(H_2bim)$ and a few crystals to the stoichiometry $Cu_{1.5}Cl_3(H_2bim)_2$.

0020-1693/88/$3.50

Only the crystals of $Cu_{1.5}Cl_3(H_2bim)_2$ were suitable for X-ray analysis. However we were unable to obtain enough compound to perform spectrophotometric measurements.

$CuCl_2(H_2bim)$ is insoluble in the common organic solvents, being soluble only in water.

### *Physical Measurements*

Electronic spectra were recorded in the range 1300–300 nm with a Perkin-Elmer Lambda 9 Spectrophotometer. Solution spectra were performed on water solutions of about $10^{-3}$ molar. Polycrystalline powder EPR spectra were recorded at room temperature at X-band (9.35 GHz) on a Varian E-9 spectrophotometer.

### *X-ray Structural Determination*

Single crystal diffraction data for $Cu_{1.5}Cl_3(H_2bim)_2$ were collected at room temperature on a Philips PW1100 automated diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 70.170$ pm). Details on crystal data, intensity collection, and refinement are reported in Table I. Lattice constants were obtained by a least-squares fit of 20 reflections in the range $10° \leqslant 2\theta \leqslant 22°$. Stationary background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections measured every 120 min did not show any systematic variation. All the crystals examined showed a net decrease of the intensities of the reflections measured at $2\theta \geqslant \approx 40°$.

TABLE I. Summary of Crystal Data, Intensity Collection and Structure Refinement

| | |
|---|---|
| Formula | $C_6H_6N_4CuCl_2 \cdot 1/2(C_{12}H_{12}N_8\text{-}CuCl_2)$ |
| Formula weight | 389.91 |
| Space group | $P21/c$ |
| $a$ (pm) | 794.0(3) |
| $b$ (pm) | 3146.8(6) |
| $c$ (pm) | 722.9(4) |
| $\beta$ (°) | 114.2(1) |
| $V$ (pm$^3$) | $1648(1) \times 10^6$ |
| $Z$ | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.571 |
| Crystal size (mm) | 0.05 × 0.12 × 0.62 |
| $\mu$(Mo K$\alpha$) | 24.40 |
| Transmission factors | 0.91–0.55 |
| Scan type | $\omega$-$2\theta$ |
| Scan width ($\Delta(2\theta)$) (°) | 0.9 + 0.3tg$\theta$ |
| Scan speed (° min$^{-1}$) | 3 |
| $2\theta$ limits (°) | 5–50 |
| Data collection range | $\pm h, k, l$ |
| No. data | 3204 |
| No. data $F_o^2 > 3\sigma(F_o^2)$ | 1188 |
| No. variables | 144 |
| $R$ | 0.063 |
| $R_w$ | 0.060 |

The $R$ factor for merging equivalent measurements was $R = 0.04$. Data were processed with use of a $p$ value of 0.03 in the calculation of $\sigma(I)$s [6]. Corrections for Lorentz and polarization effects [7] as well as for absorption [8] were applied. The structure was solved in the centrosymmetric $P21/c$ space group using the crystal structure solution program SHELXS86 by means of Patterson techniques. The computer programs used in the crystallographic calculations are listed in refs. 7–11.

A total of 1188 reflections having $F_o > 3\sigma(F_o)$ were retained during the refinement. The function minimized was $\Sigma w[|F_o| - |F_c|]^2$ with weights $w = 1.32/(\sigma^2(F_o))$. The scattering factors for the neutral atoms were taken from ref. 12, and anomalous dispertion terms for the metal atoms were included in $F_c$ [12, p. 148]. Cu, Cl and N atoms bound to copper were assigned anisotropic temperature factors, whereas all the other atoms were refined isotropically. Hydrogen atoms were introduced in calculated positions (C–H = 108 pm), and their contributions were included in $F_c$. During the last cycles of refinement one peak one electron high remained localized at 106 pm from Cu(2). The final values of the discrepancy indices, defined by $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, were $R = 0.063$ and $R_w = 0.060$. In the final least-squares cycle no shift/error ratio was higher than 0.03.

The final atomic positional parameters for the non-hydrogen atoms are listed in Table II. See also 'Supplementary Material'.

## Results and Discussion

By the reaction of hydrated $CuCl_2$ and $H_2bim$ in a 1:2 molar ratio in aqueous HCl two types of crystalline compounds were obtained. Most of the crystals correspond to the formula $CuCl_2(H_2bim)$, but a small amount of crystals having the stoichiometry $Cu_{1.5}Cl_3(H_2bim)_2$ was also obtained mixed with the main compound. As the stoichiometry does not allow us to deduce any definite stereochemistry for the latter derivative, its structure has been investigated by X-ray diffraction method.

The crystals of $Cu_{1.5}Cl_3(H_2bim)_2$ derivative contain neutral molecules $[CuCl_2(H_2bim)]$ (1), cationic $[Cu(H_2bim)_2]^{2+}$ (2) species and interspersed chloride anions in a 2:1:2 molar ratio. A drawing of the asymmetric unit showing the labelling of the atoms is shown in Fig. 1. Selected bond distances and angles are reported in Table III.

In complex 1 the copper atom is coordinated by two nitrogen atoms of a 2,2′-biimidazole molecule and by two chlorine atoms. The coordination geometry is roughly planar, the main deviation from coplanarity being given by the Cl(2) atom. It deviates

TABLE II. Positional Parameters (× $10^4$) for Non-hydrogen Atoms of $Cu_{1.5}Cl_3(H_2bim)_2$

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Cu(1) | 7132(2) | 7221(1) | 1071(3) |
| Cu(2) | 0 | 5000 | 5000 |
| Cl(1) | 8733(5) | 6626(1) | 2448(6) |
| Cl(2) | 9046(5) | 7659(1) | 3601(6) |
| Cl(3) | 7320(6) | 4435(1) | −4248(6) |
| N(1) | 4881(15) | 6898(3) | −771(18) |
| N(2) | 2049(16) | 6896(3) | −3179(18) |
| N(3) | 5473(15) | 7710(3) | −287(17) |
| N(4) | 2705(16) | 7931(3) | −2452(18) |
| N(5) | 439(16) | 4516(4) | 3385(18) |
| N(6) | −296(15) | 4236(4) | 321(19) |
| N(7) | −1876(15) | 5159(3) | 2271(18) |
| N(8) | −3044(15) | 5034(4) | −1028(19) |
| C(1) | 4324(19) | 6487(5) | −1253(23) |
| C(2) | 2588(19) | 6480(4) | −2753(22) |
| C(3) | 3490(19) | 7135(4) | −1948(21) |
| C(4) | 3789(17) | 7592(4) | −1684(21) |
| C(5) | 3760(19) | 8290(5) | −1521(24) |
| C(6) | 5443(19) | 8146(4) | −248(22) |
| C(7) | 1489(19) | 4155(4) | 3603(24) |
| C(8) | 1006(20) | 3977(5) | 1696(24) |
| C(9) | −597(19) | 4557(4) | 1419(22) |
| C(10) | −1846(19) | 4913(4) | 807(22) |
| C(11) | −3922(19) | 5393(5) | −777(23) |
| C(12) | −3195(19) | 5463(5) | 1266(23) |

by 64.4(4) pm from the Cu(1)N(1)N(3) plane, whereas Cl(1) deviates only by 3.9(4) pm from the same plane. The displacement of Cl(2) from the coordination plane may be ascribed to the interaction of this chlorine atom with a copper atom, Cu(1)' related by the symmetry operation (+*x*, 3/2 − *y*, 1/2 + *z*). The intermolecular Cl(2)....Cu(1)' interaction is as long as 280.4(5) pm and gives rise to a stepped-chain structure as shown in Fig. 2. The Cu(1)–Cl(2)–Cu(1)' bridge angle is 103.5(3)°. Even if the out-of-plane Cu....Cl interaction is considerably longer than the analogous in-plane bond length (280 *versus* 225–230 pm), the coordination around copper(II) can be better described as an elongated square pyramid. As a matter of fact the ratio between the mean in-plane Cu–Cl distance and the out-of-plane Cu–Cl distance (usually referred to as the tetragonality of the coordination geometry) is in the range found in tetragonally distorted mononuclear copper complexes [13]. Bond distances and angles within the coordination sphere and within the ligand molecule are in the normal range [2, 5c].

In complex 2 the copper atom lies on an inversion centre and is four coordinated by the nitrogen atoms of two symmetry related 2,2'-biimidazole molecules in a strictly planar environment. Bond distances and angles within the $[Cu(H_2bim)_2]^{2+}$ species do not differ significantly from the corresponding ones in complex 1. The shortest contacts of Cl(3) with the atoms of complex 2 are reported in Table IV. Two nearest neighbour Cl(3) atoms are at 298.8(5) pm from the Cu(2) atom and are involved in hydrogen bonding with the >N–H groups of adjacent molecules. A schematic view of the crystal packing is shown in Fig. 3.

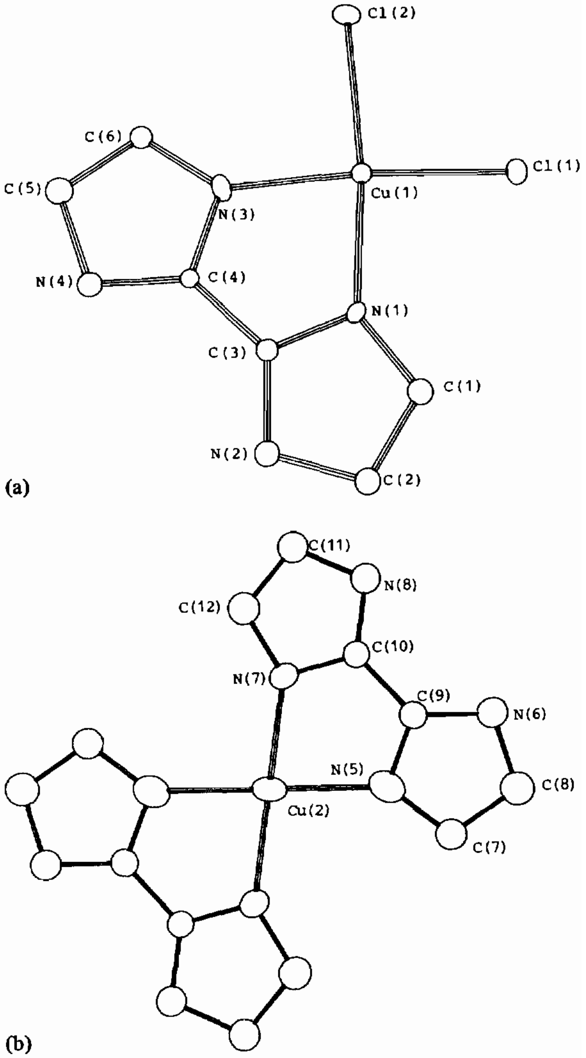

Fig. 1. ORTEP views of (a) $[CuCl_2(H_2bim)]$ and (b) $[Cu(H_2bim)_2]^{2+}$ showing the atom-numbering scheme.

The structure of complex 1 found in $Cu_{1.5}Cl_3(H_2bim)_2$ is presumably the same as that of $CuCl_2(H_2bim)$ obtained as the main product from the reaction of copper chloride and the ligand (see 'Experimental'), the stoichiometry being the same. This main product is insoluble in the common organic solvents presumably because of its polymeric structure with bridging chlorine.

Electronic spectra of $CuCl_2(H_2bim)$ both in the solid state and in water solution are practically the

TABLE III. Selected Interatomic Distances (pm) and Angles (°) for $[CuCl_2(H_2bim)]$ (i) and $[Cu(H_2bim)_2]^{2+}$ (ii)

| | | | |
|---|---|---|---|
| (i) | | | |
| Coordination sphere | | | |
| Cu(1)–Cl(1) | 225.4(4) | Cl(1)–Cu(1)–Cl(2) | 94.4(1) |
| Cu(1)–Cl(2) | 229.7(4) | Cl(1)–Cu(1)–N(1) | 93.4(3) |
| Cu(1)–N(1) | 201(1) | Cl(2)–Cu(1)–N(3) | 91.0(4) |
| Cu(1)–N(3) | 200(1) | Cl(1)–Cu(1)–N(3) | 173.9(3) |
| Cu(1)–Cl(2) | 280.4(5) | N(1)–Cu(1)–Cl(2) | 161.5(4) |
| | | N(1)–Cu(1)–N(3) | 80.6(4) |
| | | Cl(2)–Cu(1)–Cl(2)′ | 94.1(4) |
| Ligand | | | |
| N(1)–C(1) | 136(2) | N(1)–C(3)–N(1) | 112(1) |
| N(1)–C(3) | 132(2) | N(1)–C(1)–N(2) | 110(1) |
| N(2)–C(3) | 135(2) | N(1)–C(3)–C(4) | 115(1) |
| N(2)–C(2) | 137(2) | N(2)–C(2)–C(1) | 107(1) |
| N(3)–C(4) | 136(2) | N(2)–C(3)–C(4) | 133(1) |
| N(3)–C(6) | 137(2) | N(3)–C(4)–N(4) | 111(1) |
| N(4)–C(4) | 134(2) | N(3)–C(4)–C(3) | 115(1) |
| N(4)–C(5) | 140(2) | C(4)–N(3)–C(6) | 106(1) |
| C(1)–C(2) | 136(2) | N(3)–C(6)–C(5) | 110(1) |
| C(3)–C(4) | 146(2) | N(4)–C(4)–C(3) | 134(1) |
| C(5)–C(6) | 135(2) | N(4)–C(5)–C(6) | 107(1) |
| | | C(1)–N(1)–C(3) | 106(1) |
| | | C(2)–N(2)–C(3) | 106(1) |
| | | C(4)–N(4)–C(5) | 106(1) |
| (ii) | | | |
| Coordination sphere | | | |
| Cu(2)–N(5) | 203(1) | N(5)–Cu(2)–N(7) | 81.6(5) |
| Cu(2)–N(7) | 199(1) | | |
| Ligand | | | |
| N(5)–C(7) | 138(2) | N(5)–C(7)–C(8) | 108(1) |
| N(5)–C(9) | 132(2) | N(5)–C(9)–N(6) | 112(1) |
| N(6)–C(8) | 137(2) | N(5)–C(9)–C(10) | 117(1) |
| N(6)–C(9) | 136(2) | N(6)–C(9)–C(10) | 131(1) |
| N(7)–C(10) | 132(2) | N(7)–C(12)–C(11) | 110(1) |
| N(7)–C(12) | 139(2) | N(7)–C(10)–C(9) | 116(1) |
| N(8)–C(10) | 133(2) | N(7)–C(10)–N(8) | 113(1) |
| N(8)–C(11) | 138(2) | N(8)–C(11)–C(12) | 105(1) |
| C(7)–C(8) | 139(2) | N(8)–C(10)–C(9) | 130(1) |
| C(9)–C(10) | 144(2) | C(7)–C(8)–N(6) | 107(1) |
| C(11)–C(12) | 137(2) | C(9)–N(6)–C(8) | 106(1) |
| | | C(9)–N(5)–C(7) | 106(1) |
| | | C(10)–N(8)–C(11) | 107(1) |
| | | C(10)–N(7)–C(12) | 104(1) |

TABLE IV. Selected Short Bond Contacts in $[Cu(H_2bim)_2]Cl_2$

| A | B | Symmetry related B atom | d (pm) |
|---|---|---|---|
| Cu(2) | Cl(3) | $x - 1, y, 1 + z$ | 298.8(5) |
| Cu(2) | Cl(3) | $1 - x, 1 - y, -z$ | 298.8(5) |
| Cl(3) | N(6) | $1 + x, y, z$ | 313(1) |
| Cl(3) | N(8) | $1 + x, y, z$ | 310(1) |
| Cl(3) | H(6) | $1 + x, y, z$ | 216(1) |
| Cl(3) | H(8) | $1 + x, y, z$ | 209(1) |

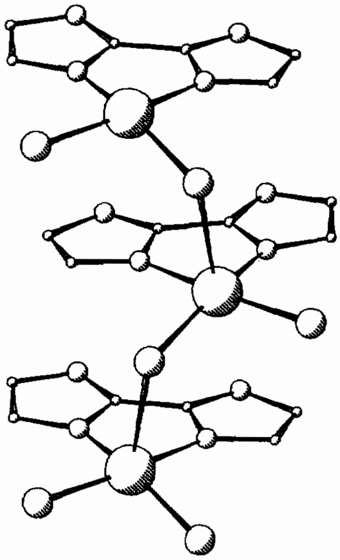

Fig. 2. Drawing of the polymeric structure of $[CuCl_2(H_2bim)]$ with chlorine bridge.

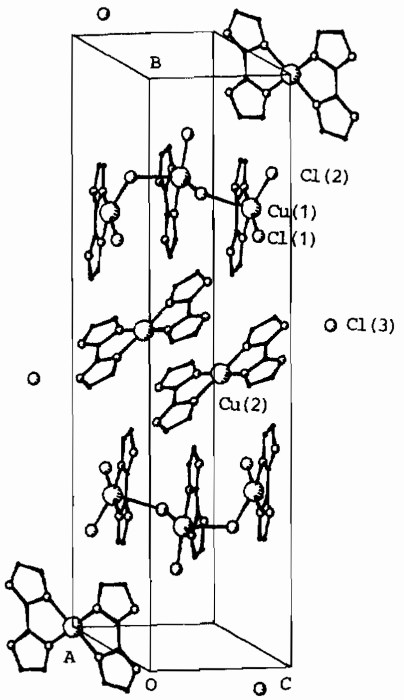

Fig. 3. Schematic view of the crystal packing of $Cu_{1.5}Cl_3(H_2bim)_2$. Hydrogen atoms are omitted.

same with a single broad band centered at 700 nm ($\epsilon = 31.5$ cm$^2$ mmol$^{-1}$).

Polycrystalline powder EPR spectra can be interpreted with a rhombic $S = \frac{1}{2}$ spin Hamiltonian with $g_1 = 2.21$, $g_2 = 2.09$, $g_3 = 2.06$. Both the electronic and EPR spectra are due to complex **1** which is present in the largest quantity and are consistent with a distorted planar coordination of copper with a negligible interaction with the axial chlorine atom at 280 pm.

## Supplementary Material

Thermal parameters and positional parameters of the hydrogen atoms (Tables SI and SII, respectively) and listing of the observed and calculated structure amplitude are available from the authors on request.

## References

1 F. Holmes, K. M. Jones and E. G. Torrible, *J. Chem. Soc.*, 4790 (1961).

2 A. D. Mighell, C. W. Reimann and F. A. Mauer, *Acta Crystallogr., Sect. B, 25,* 60 (1969); S. W. Kaiser, R. B. Saillant, W. M. Butler and P. G. Rasmussen, *Inorg. Chem., 15,* 681 (1976); I. G. Dance, A. S. Abushamleh and H. A. Goodwin, *Inorg. Chim. Acta, 43,* 217 (1980).

3 O. Kahn, *Struct. Bonding, (Berlin), 68,* 89 (1987).

4 H. C. Freeman, in G. L. Eichorn (ed.), 'Inorganic Biochemistry', Elsevier, Amsterdam, 1975.

5 (a) M. S. Haddad, E. N. Duesler and D. N. Hendrickson, *Inorg. Chem., 18,* 141 (1979); (b) E. E. Bernarducci, P. K. Bharadwaj, R. A. Lalancette, K. Krogh-Jespersen, J. A. Potenza and H. J. Schugan, *Inorg. Chem., 22,* 3911 (1983); (c) C. Kirchner and B. Krebs, *Inorg. Chem., 26,* 3569 (1987).

6 P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem., 6,* 197 (1967).

7 J. M. Stewart, F. A. Kundall and J. C. Baldwin, 'X-ray 72 System of Programs', *Technical Report TR 192,* University of Maryland, College Park, Md., 1972.

8 G. M. Sheldrick, 'SHELX 76', system of computing programs, University of Cambridge, U.K., 1976.

9 C. K. Johnson, *Report ORNL-3794,* Oak Ridge Natl. Lab., Oak Ridge, Tenn., U.S.A., 1965.

10 M. Nardelli, 'PARST', *Computer and Chemistry, 7,* 95 (1983).

11 G. M. Sheldrick, 'SHELXS 86', in G. M. Sheldrick, C. Krüger and R. Goddard (eds.), 'Crystallographic Computing 3', Oxford University Press, U.K., 1985, p. 175.

12 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K., 1974, p. 71.

13 B. J. Hathaway, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), 'Comprehensive Coordination Chemistry', Pergamon Press, Oxford, 1987, p. 603.